

AD-A132-050

AEROSOL DIRECT FLUORINATION SYNTHESIS: ALKYL HALIDES I
NEOPENTYL CHLORIDE..(U) TENNESSEE UNIV KNOXVILLE DEPT
OF CHEMISTRY J J ADCOCK ET AL. 30 JUL 83 TR-8

1/0

UNCLASSIFIED

N00014-77-C-0685

F/G 7/4

NL

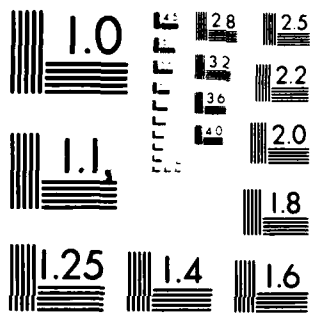
END

DATE

FILED

9 83

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

17

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0685

Task No. NR 053-669

TECHNICAL Report No. 8

MS 3-118C REVISED

AEROSOL DIRECT FLUORINATION SYNTHESSES: ALKYL HALIDES I, NEOPENTYL
CHLORIDE AND BROMIDE, FREE RADICALS VERSUS CARBOCATIONS

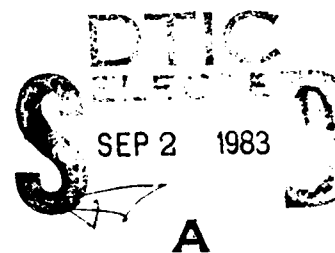
by

James L. Adcock
William D. Evans and
Lilly Heller-Grossman

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

July 30, 1983

Prepared for Publication in the
Journal of Organic Chemistry



Reproduction in whole or in part is permitted for any purpose of the United
States Government

This document has been approved for public release and sale; its distribution
is unlimited

ADA 132050

DTIC FILE COPY

38 04 03 140

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 8	2. GOVT ACCESSION NO. A132 050	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Low Temperature Fluorination of Aerosol Suspensions of Hydrocarbons Utilizing Elemental Fluorine- "Aerosol Direct Fluorination Syntheses: Alkyl Halides 1, Neopentyl Chloride and Bromide, Free Radicals Versus Carbocations.		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) James Adcock, William D. Evans and Lilly Heller-Grossman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Tennessee - Knoxville Knoxville, TN 37996-1600		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0685
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-669
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE July 30, 1983
		13. NUMBER OF PAGES 28
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aerosol, Direct Fluorination, Elemental Fluorine, Alkyl Halides, Perfluoroalkyl Halides, Carbocations.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Aerosol direct fluorination of neopentyl chloride produces perfluoro-neopentyl chloride in 74% yields. Analogous fluorination of neopentyl bromide produces perfluoroisopentane in 63% yield. Data is presented which supports a carbocation rearrangement in the fluorination of neopentyl bromide. The carbocations are presumed to arise from disproportionation of neopentyl bromide fluorides.		

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MS 3-118C REVISED

AEROSOL DIRECT FLUORINATION SYNTHESSES: ALKYL HALIDES I, NEOPENTYL
CHLORIDE AND BROMIDE, FREE RADICALS VERSUS CARBOCATIONS

by

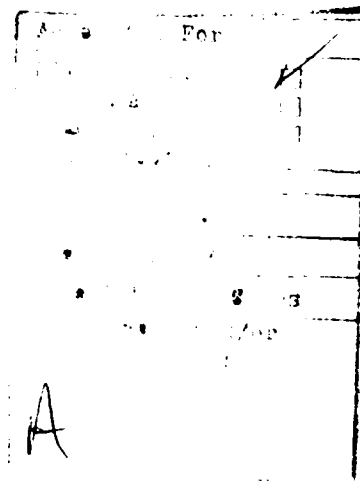
James L. Adcock,*
William D. Evans
Lilly Heller-Grossman

Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

Submitted to
Journal of Organic Chemistry

ABSTRACT

Aerosol direct fluorination of neopentyl chloride produces perfluoro-neopentyl chloride in 74% yields. Analogous fluorination of neopentyl bromide produces perfluoroisopentane in 63% yield. Data is presented which supports a carbocation rearrangement in the fluorination of neopentyl bromide. The carbocations are presumed to arise from disproportionation of neopentyl bromine fluorides.



Aerosol Direct Fluorination Syntheses: Alkyl Halides I, Neopentyl
Chloride and Bromide-Free Radicals versus Carbocations

by

J. L. Adcock, W. D. Evans and L. H. Grossman

The direct fluorination of alkyl halides to perfluoroalkyl halides would provide a method of obtaining specific fluorocarbons in which the site for further reaction has been preselected prior to fluorination. The fluorination of chloroalkanes by metathesis using HF, F⁻ or SbF₃ does not provide for prior selection of residual halogens although specific fluorocarbon halides may be obtained as products.¹ Several investigators have shown the feasibility of maintaining carbon-chlorine bonds during cobalt trifluoride fluorinations,² and during electrochemical fluorinations.³ There has to our knowledge however, been only one published report of an elemental direct fluorination of an alkyl halide to a perfluoroalkyl halide.⁴ In this paper we would like to demonstrate the facility of maintaining a primary chlorine substituent during aerosol direct fluorinations. The stability of this chlorine substituent to both elemental and photochemically generated atomic fluorine at 20°C is exceptional. The stability of bromine substituents is, however, very low and they tend to be oxidized by elemental fluorine at temperatures as low as -60°C. Generation of carbocations is indicated in the fluorinations of alkyl bromides but not in the fluorinations of alkyl chlorides.

Results and Discussions

The aerosol direct fluorination process has been described in detail elsewhere.⁵ Two major elements of the process involve contact of elemental fluorine with a finely-divided-particulate reactant aerosol over a gradual temperature and fluorine concentration gradient followed by "photochemical finishing" of the highly fluorinated product by ultraviolet irradiation of the effluent under ambient fluorine concentration conditions at ca. 20°C. The two steps may be separated for analytical purposes simply by making control runs with the mercury lamp off. The reactant aerosol is formed by adsorption/condensation of hydrocarbon onto a sodium fluoride preaerosol.

Initially two prototype molecules for probing the feasibility of the alkyl halide reactions were chosen because of their sensitivity to mechanistic reaction paths and their expected, near-ideal, reactor-process behavior. The first candidate, neopentyl chloride, was prepared by the method of Wiley, et. al. from neopentyl alcohol.⁶ It was shown to be uncontaminated with isopentyl chloride by gas chromatography and by proton nuclear magnetic resonance. The aerosol fluorination of this molecule was uneventful and produced product in 79.6% purity (glc assay) direct from the reactor trap. Isolated yields of pure perfluoroneopentyl chloride were 74% of theoretical. The remaining 20% of the material in the product trap was composed of approximately 20% F-isobutane, 20% F-isobutyl chloride, 40% F-pivaloyl fluoride and the remainder numerous very small peaks with retention times greater than F-neopentyl chloride.

The second candidate, neopentyl bromide, was produced also by the method of Wiley, et. al.,⁶ and was shown to be free of isopentyl bromide by gas chromatography and proton nmr. The aerosol fluorination of neopentyl bromide was carried out under conditions similar to those for the chloride. The

product consisted of 80% F-isopentane, 10% F-isobutane, elemental bromine and lesser products.

The most significant result of the neopentyl bromide fluorinations is the near total rearrangement of the neopentyl moiety to the isopentyl. Such rearrangements must certainly occur early in the fluorination because low fluorine, control runs without photochemical finishing [Rxns (2) + (5), Table 1] produce exclusively rearranged products or unreacted starting material. Reactions 2 through 5 represent stepwise reductions in neopentyl bromide to fluorine mole ratios from approximately 1:12 to 1:1. Product distributions for neopentyl bromide reactions (1) through (5) are also given in Table 1.

The major product isolated at 1:1 stoichiometry (Rxn 5) is 2-methyl-2-butene (9). As the fluorine to neopentyl bromide ratio is increased (Rxn 4) 2-methyl-2-butene (9) disappears and 2,3-difluoro-2-methylbutane (10) becomes the prevalent product. However "abnormal" products having the geminal difluoromethylene group are collectively of near equal prevalence. These abnormal products increase as the relative amount of fluorine increases (Rxns 3 and 2) and the amount of 2,3-difluoro-2-methylbutane actually decreases in reaction 2. Compounds having this geminal difluorosubstitution (Cmpds 3, 4, 5, 6 and 7 Table 1) are classified "abnormal" because none are the statistically probable products expected from fluorine attack on the products (9 and 10) prevalent at the lowest stoichiometries.

The facility with which neopentyl cations rearrange to isopentyl cations is a well known phenomenon.⁷ It is also known that neopentyl radicals do not show a pronounced tendency to rearrange.⁸ This leads to the inescapable conclusion that the fluorination of neopentyl bromide must produce intermediate carbocations, although highly polar species or carbene type

TABLE 1

RESULTS OF AEROSOL FLUORINATIONS OF NEOPENTYL BROMIDE

Reaction Number		(1) ^(a)	(2)	(3)	(4)	(5)
Fluorine:Hydrocarbon mole ratio		105	12	4	2.5	1
Prod No.	Product Name	Product Distribution ^b				
<u>1</u>	Neopentyl Bromide ^(c)	-	-	15	28	50
<u>3</u>	3,3-Difluoro-2-methylbutane	-	18	14	6	-
<u>4</u>	2,3,3-Trifluoro-2-methylbutane	-	10	2	4	-
<u>5</u>	1,3,3-Trifluoro-2-methylbutane	-	18	6	2	-
<u>6</u>	3,3,4-Trifluoro-2-methylbutane	-	}(e) 16	5	5	-
<u>7</u>	1,3,3,-Trifluoro-2-fluoromethylbutane	-				
<u>8</u>	F-Isopentane	80	-	-	-	-
<u>9</u>	2-Methyl-2-butene	-	-	-	-	30
<u>10</u>	2,3-Difluoro-2-methylbutane	-	11	20	20	-
	F-Isobutane	10	-	-	-	-
	Residual Peaks ^(d)	10	27	38	35	20

(a) Photochemical stage operative here only.

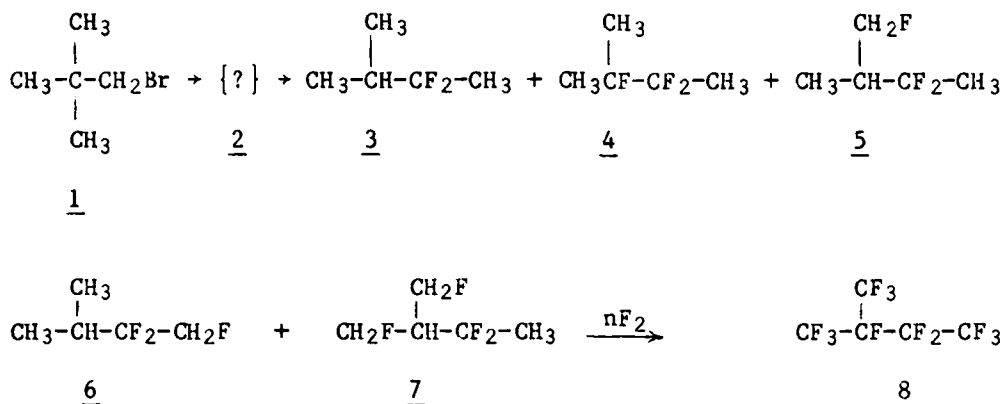
(b) Area Percent of total injection by peak integration of the thermal conductivity gas chromatogram.

(c) Unreacted starting material.

(d) Small peaks in gas chromatogram.

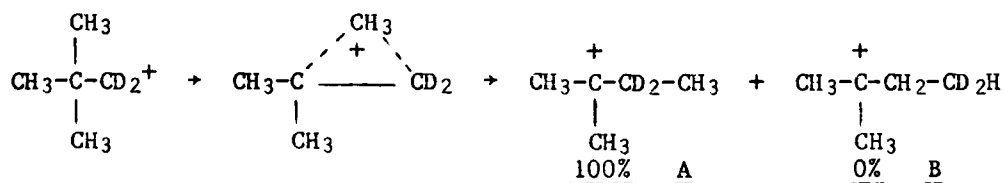
(e) Inseparable mixture, tentative identification by ¹⁹F and ¹H NMR.

intermediates cannot be totally eliminated. Furthermore these carbocations and their precursor intermediate(s), {?} (2) Scheme I, must account for the "abnormal" fluorine products (3-7) containing the difluoromethylene group [Scheme I].



Scheme I

The nature of these intermediates are not known but their behavior bears a striking resemblance to the rearrangements of the neopentyl cation observed by Skell, et al. [Scheme II].⁷ Skell, et. al. observed that all derived products of the rearrangement were consistent with the deuterium label in the 3-position, i.e. exclusively derived from A.



Scheme II

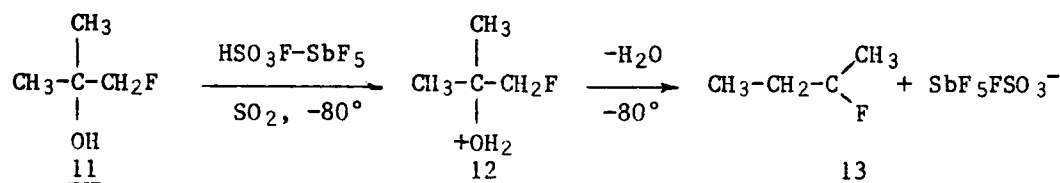
A protonated cyclopropane derivative was thus discounted because it could cleave either of two ways producing t-amyl derivatives consistent with the deuterium label in the 4-position (derived from B) also, which was not

observed. Karabatsos, et. al. observed this rearrangement of neopentyl cations using a ^{13}C label and obtained the same result.¹⁰

One hypothetical scheme (Scheme III) which not only provides a reasoned approach to all of the products produced, but also addresses the product shift as the fluorine stoichiometry is increased, is in effect two schemes. The basic postulate supported by reaction 5 (Table 1) is that fluorine attacks only the bromine and that depending on the stoichiometry either (or both) an alkylbromine difluoride (2a') or an alkylbromine tetrafluoride (2a) is formed. Conceivably 2a' may disproportionate giving the known inter-halogen anion, BrF_2^- and the carbocation 2b' which through Scheme II produces the t-amyl cation "A" and by loss of a proton 2-methyl-2-butene (9) the largest single product in reaction 5. As the fluorine to alkylbromide ratio is increased significant amounts of the alkylbromine tetrafluoride (2a) are produced leading to formation of the fluorinated carbocation (2b) which through Scheme II produces the fluorinated t-amyl cation (2c). The major product in reaction 4, 2,3-difluoro-2-methylbutane, may be produced by fluorine addition to 9 or by fluoride ion trapping of 2c. Both routes "A" and "B" are probably operating. As the fluorine:alkylbromide ratio is increased further (reactions 3 and 2) the proportion of route "A" is diminished over route "B" since the other products produced by route "B" alone (3, 4 and 5) are increasing while that product (10) produced by route(s) "A" (and "B") is diminishing. It is also likely that the beta fluorinated t-amyl cation (2c) contributes less to product 10 than expected because of its ready rearrangement (1,2-hydride shift) to the alpha fluorinated secondary butyl cation (2d). The sigma inductive destabilization of (2c) by the beta fluorine coupled to the resonance (π -donor) stabilization of (2d) by

the alpha fluorine inverts the usual $1^\circ < 2^\circ < 3^\circ$ carbocation stabilization.¹¹ Fluoride ion trapping of (2d) leads to 3,3-difluoro-2-methylbutane (3), which by statistically-directed, radical-chain, direct fluorination leads to product (5), 1,3,3-trifluoro-2-methylbutane and to the tentatively identified 3,3,4-trifluoro-2-methylbutane (6) and 1,3,3-trifluoro-2-fluoro-methylbutane (7) and, ultimately, to F-isopentane (8). Together products 3, 5 and the 6, 7 mixture make up 52% of the total products in reaction 2 with product 4, 2,3,3-trifluoro-2-methylbutane produced by proton abstraction from 2c and/or 2d followed by fluorine addition to the olefin produced, makes an additional 10% of the total.

Support for this hypothesis is provided by Olah and Bollinger in which the protonation studies of *i*-fluoro-2-methyl-2-propanol in "magic acid," $\text{HSO}_3\text{F-SbF}_5/\text{SO}_2$, at -80°C produced the results shown in Scheme IV.¹¹



Scheme IV

The only carbocation detected in this system was 13 although the chloro analog produced the chloro-*t*-butyl cation. Carbocation 13 requires, in effect, two hydride shifts and one methide shift to occur for it to be produced from a transient fluoro-*t*-butyl cation which was not detected by Olah and Bollinger.¹¹ The only unsubstantiated or unsupported parts of our hypothesis (Scheme III) is the formation of 2a and 2a' and their "disproportionation" to 2b and 2b' respectively. The formation of perfluoroalkyl bromine tetrafluorides is however documented.¹² Although a potential route

"C" from 2a' to 2b is shown in Scheme III our evidence does not support or require it, although it cannot be eliminated a priori. It is also problematical whether 2a' will have sufficient lifetime to interact with a second mole of fluorine to form 2a, or whether two moles of fluorine must act in concert as implied by route "B" Scheme III. Whatever the mechanism insufficient data exist to more than simply pose the question. The solution of this problem might be obtained through matrix isolation studies. It is however clear that fundamental differences in the mode of fluorine attack on alkyl chlorides and bromides exist and that the consequences will likely involve "carbocation" type rearrangements of the organic substituent.

Acknowledgement. This work was supported in part by the Office of Naval Research whose support is gratefully acknowledged. Supplementary Material Available. Detailed reaction parameters, full characterization of compounds 3-8 (7 pages). Ordering information is given on any current masthead page.

EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.⁵ Workup of products following removal of hydrogen fluoride and possibly fractional collection at ambient pressures using in-line cold traps, consisted of vacuum line fractionation; infrared assay of fractions; gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed, Chromosorb p conditioned at 225°C (12 hrs) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 250°C (12 hrs). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller) all products of significance were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization (CH₄ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and ¹H and ¹⁹F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl₃ with 1% CFCl₃ internal standard. Elemental Analyses where necessary are performed by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y. Detailed reaction parameters and compound characterizations (7 pages) are available as Supplementary Material, ordering information is given on any current masthead page.

Aerosol Fluorination of Neopentyl Chloride: 1-Chloro-2,2-dimethylpropane was prepared by the method of Wiley, *et. al.* from neopentyl alcohol.⁶ Its vapor pressure at -10°C is such that a flow of 85 mL/m helium through -50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.38 g/hr (3.6 mmol/h). Details of the aerosol fluorination parameters are available as supplementary materials. For a 3h photochemically finished run, 2.659g of crude product was collected which when vacuum

line fractionated [-131°C (2.56g), -196°C (0.09g discarded)] and gas chromatographically purified on the SE-52 column ($15^{\circ}\text{C}/5\text{ m}$; $10^{\circ}\text{C}/\text{m}$ to 75°C ; $50^{\circ}\text{C}/\text{m}$ to $150^{\circ}\text{C}/7\text{ m}$) produced 2.03g of F-neopentyl chloride 79.6% of the crude material collected, 74% yield based on calculated throughput. Characterization by ^{19}F NMR gave $\delta_{\text{CF}_3} = -64.18\text{ ppm}$ (t) [9], $\delta_{\text{CF}_2\text{Cl}} = -52.29\text{ ppm}$ (dectet) [2], $J = 10.7\text{ hz}$. Elemental Analyses: Calculated for $\text{C}_5\text{F}_{11}\text{Cl}$: %C 19.72, %F 68.63; Found %C 19.67, %F 68.60. Detailed IR, Mass Spec (CI, EI) are available as supplementary material.

Aerosol Fluorination of Neopentyl Bromide: 1-Bromo-2,2-dimethylpropane was prepared by the method of Wiley, et. al. from neopentyl alcohol.⁶ Its vapor pressure at -10°C is such that a flow of 25 mL/m helium through -20 mL of the material contained in a sparge tube evaporator produces a throughput of 1.4 mmol/h. Details of the aerosol fluorination parameters are available as Supplementary Material. Five fluorination runs were carried out differing mainly in the photochemical finishing (i.e. run #2-#5 uv lamp off), and the fluorine to hydrocarbon stoichiometry (Table 1). All products were vacuum line fractionated (-131°C , -196°C discarded) and the -131°C trap separated gas chromatographically on the SE-52 column ($10^{\circ}\text{C}/4\text{ m}$; $2^{\circ}/\text{m}$ up to $55^{\circ}\text{C}/1\text{ m}$; $50^{\circ}\text{C}/\text{m}$ to $125^{\circ}\text{C}/10\text{ m}$).

The photochemically finished, two-hour run (Rxn. 1) produced 0.629g of crude product after removal of elemental bromine with the following product distribution: 80% F-isopentane (62.5% yield), 10% F-isobutane and 10% other unidentified lesser products. F-Isopentane collected displayed spectra identical to the infrared and ^{19}F NMR spectra published.^{13,14} Detailed Mass Spectra, Infrared and ^{19}F NMR are available from Supplementary Materials.

The runs without the ultraviolet lamp (Rxns. 2-5, Table 1) produced

similar quantities of crude product containing elemental bromine with the product distributions listed. Characterizations of intermediate products are available from supplementary materials; 3,3-Difluoro-2-methylbutane (3),¹⁵ 2,3-Difluoro-2-methylbutane (10)¹⁶ are known compounds. 2,3,3-Trifluoro-2-methylbutane (4) and 1,3,3-Trifluoro-2-methylbutane (5) have not been previously characterized.

REFERENCES

1. (a) Henne and Trott, J. Amer. Chem. Soc., 1947, 69, 1820. (b) McBee, Wiseman and Bachman, Ind. Eng. Chem., 1947, 39, 415. (c) Henne and Newby, J. Amer. Chem. Soc., 1948, 70, 130. (d) Henne and Ruh, J. Amer. Chem. Soc., 1947, 69, 279.
2. (a) R. D. Bagnall, W. Bell and K. Pearson, J. Fluor. Chem., 1977, 9, 359-375. (b) R. E. Banks, R. N. Haszeldine and Walton, J. Chem. Soc., 1963, 5581.
3. (a) H. M. Fox, F. N. Ruehler and W. V. Childs, J. Electrochem Soc., 1971, 118, 1246-9. (b) B. H. Ashe and W. V. Childs, U.S.P. 3,720,597 (1973). (c) T. Abe and S. Nagase, J. Fluor. Chem., 1979, 13, 519-530.
4. M. Schmeisser, K. P. Ehlers and P. Sartori, Angew. Chem. (Int. Ed.), 1967, 6, 627.
5. J. L. Adcock, K. Horita and E. B. Renk, J. Amer. Chem. Soc., 1981, 103, 6937-47.
6. G. A. Wiley, R. L. Herskowitz, B. M. Rein and B. C. Chung, J. Amer. Chem. Soc., 86, 964.
7. J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill Book Co., New York, 1968 pp. 781-795.
8. F. C. Whitmore, A. N. Popkin, H. J. Bernstein and J. P. Wilkins, J. Amer. Chem. Soc., 1941, 63, 124-7.
9. P. S. Skell, I. Starer and A. P. Krapcho, J. Amer. Chem. Soc., 1960, 82, 5257-8.
10. G. J. Karabatsos and J. D. Graham, J. Amer. Chem. Soc., 1960, 82, 5250-1.
11. G. A. Olah and J. M. Bollinger, J. Amer. Chem. Soc., 1968, 90, 947-53.
12. M. H. Habibi and L. C. Sams, J. Fluor. Chem., 1981, 18, 277-280.
13. Sadtler, Infrared #41640P (1967).

14. R. D. Dresdner, F. N. Thimoe and J. A. Young, J. Amer. Chem. Soc., 1960, 82, 5831.
15. V. I. Golikov, A. M. Aleksandrov, L. A. Alekseeva, and L. M. Vagupol'skii, Zhurnal Organicheskoi Khimii, 1974, 10, 297-99 (In Translation UDC 7.412.22+463.4).
16. W. J. Middleton, J. Org. Chem., 1975, 40, 574-8.

APPENDIX I

Supplementary Material

Characterization of Intermediate Products

SUPPLEMENTARY MATERIAL

TABLE A
TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS

Starting Compound	Fluorine Flow ml./m		Helium Diluent ml./m		Reaction Temp. °C		Helium Carrier ml./m	Hydrocarbon Throughput millimoles/hr (H.C. carrier)	Overall ^a Stoichiometry he:F ₂	Percent F ₂ Conc. final stage	Reactor Volume (a length)	Reaction Time Sec.
	Reactor Mod. 1	Reactor Mod. 2	Reactor Mod. 1	Reactor Mod. 2	Reactor Mod. 1	Reactor Mod. 2						
Neopentyl Chloride	20	20	20	80	-45°	-30°	1000	3.60 (85)	1:41	4.3%	1355	59
Neopentyl Bromide(1)	20	20	60	60	-40°	-30°	1000	1.4 (25)	1:105	4.7%	1355	53
Neopentyl Bromide(2)	20	10	120	100	-40°	-30°	1000	1.10 (150)	1:12	3.2%	1355	
Neopentyl Bromide(3)	1.7	-	100	-	-48°	-30°	1000	1.2 (20)	1:4	0.15%	1355	
Neopentyl Bromide(4)	1.4	-	100	-	-40°	-30°	1000	1.4 (25)	1:2.5	9.12%	1355	
Neopentyl Bromide(5)	0.6	-	100	-	-40°	-30°	1000	1.4 (25)	1:1	9.57%	1355	

^a 1 ml./min F₂ delivers 2.44 millimoles/hr. F₂

^b Neopentyl Bromide (2)-(5) run with photochemical stage lamp off.

Supplementary Material

TABLE B

CHARACTERIZATION OF AEROSOL FLUORINATION PRODUCTS

F-Neopentyl Chloride:

Infrared (cm^{-1}): 1320(sh), 1302(vs), 1294(vs), 1239(m), 1008(s), 880(m), 773(w), 750(dblt. m).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 287 (10) $\text{C}_5\text{F}_{10}^{37}\text{Cl}$; 285 (44) $\text{C}_5\text{F}_{10}^{35}\text{Cl}$; 269 (39.7) C_5F_{11} ; 247 (95.5) $\text{C}_5\text{F}_9\text{O}$ or $\text{C}_5\text{F}_8^{35}\text{Cl}$ (? ^{37}Cl); 181 (100) C_4F_7 ; 87 (21) $\text{CF}_2^{37}\text{Cl}$; 85 (70) $\text{CF}_2^{35}\text{Cl}$; 69 (38) CF_3 .

EI (70eV): 285 (.3) $\text{C}_5\text{F}_{10}^{35}\text{Cl}$; 269 (20) C_5F_{11} ; 181 (31) C_4F_7 ; 87 (19) $\text{CF}_2^{37}\text{Cl}$; 85 (60) $\text{CF}_2^{35}\text{Cl}$; 69 (100) CF_3 .

^{19}F NMR ($\phi_{\text{CFCl}_3} \equiv 0$ ppm) [Integ]

$\phi_{\text{CF}_3} = -64.18$ ppm (t) [9]

$J = 10.7$ hz.

$\phi_{\text{CF}_2\text{Cl}} = -52.29$ ppm (dectet) [2]

Elemental Analyses: $\text{C}_5\text{F}_{11}\text{Cl}$

Calc. %C 19.72 %F 68.63

Observed %C 19.67 %F 68.60

TABLE B (CONTINUED) (2)

F-Isopentane:

Infrared (cm^{-1}):^a 1260(sh), 1255(vs), 1225(vs), 1147(mw), 1090(w),
1060(vw), 980(m), 930(w), 888(m), 720(m), 635(vw),
610(vw), 525(w)

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 182 (100.0) $\text{C}_4\text{F}_7\text{H}$; 136 (36.5) C_5F_4 ; 132 (51.6)
 $\text{C}_3\text{F}_5\text{H}$; 69 (50.3) CF_3 .

EI (70eV): 269 (5.5) C_5F_{11} , M-F; 219 (1.6) C_4F_9 ; 200 (2.5)
 C_4F_8 ; 181 (11.8) C_4F_7 ; 150 (4.5) C_3F_6 ; 131 (21.6)
 C_3F_5 ; 119 (34.7) C_2F_5 ; 100 (61.6) C_2F_4 ; 69 (100) CF_3 .

^{19}F NMR ($\phi\text{CFCl}_3 \equiv 0$ ppm), CDCl_3)^b $\text{CF}_3\text{-CF}_2\text{-CF}(\text{CF}_3)_2$
a b c d

$\phi_a = -81.2$ ppm (undecet) [3] $J_{ac} = 1.47$ $J_{ab} = ?^c$

$\phi_d = -72.92$ ppm (nonet•d) [6] $J_{ad} = 5.86$ Hz $J_{cd} = 1.47$ Hz

$\phi_b = -119.9$ ppm (heptet•d) [2] $J_{bd} = 10.99$ Hz

$\phi_c = -187.4$ ppm (mult) [1] $J_{bc} = 2.93$ Hz

(a) Sadtler, Infrared # 41640P(1967).

(b) R. D. Dresdner, F. N. Thimoe and J. A. Young, J. Amer. Chem. Soc., 1960, 82, 5831.

(c) Some uncertainties exist in coupling constants because $1.47 \times 2 = 2.94$, $2.93 \times 2 = 5.86$.

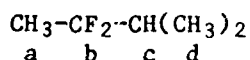
TABLE B (CONTINUED)(3)

3,3-Difluoro-2-methylbutane:

Infrared (cm^{-1}): 2980(s), 2900(m), 1480(m), 1390(s), 1360(w), 1260(s)
 1200(sh,s), 1160(vw), 1110(s), 1050(m), 920(s), 880(w),
 730(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 125 (0.6) $\text{C}_5\text{H}_{10}\text{F}_2 + \text{CH}_5^+$, 107 (0.7) $\text{C}_5\text{H}_9\text{F}_2$,
89 (100) $\text{C}_5\text{H}_{10}\text{F}$, 69 (2.1) C_5H_9 .
 EI (70eV): 93 (13.5) $\text{C}_4\text{H}_7\text{F}_2$; 78 (2.0) $\text{C}_3\text{H}_4\text{F}_2$; 77 (7.6) $\text{C}_3\text{H}_3\text{F}_2$;
 69 (18.4) C_5H_9 ; 65 (69.7) $\text{C}_2\text{F}_2\text{H}_3$; 47 (8.2) $\text{C}_2\text{H}_4\text{F}$;
43 (100) C_3H_7 .

 $^{19}\text{F} + ^1\text{H}$ NMR^{d,e}

$\delta_a = 1.51$ ppm (t) $J_{ab} = 18.8$ hz
 $\delta_c = 1.5-2.15$ ppm (mult)
 $\delta_d = 1.0$ ppm (d) $J_{cd} = 6.83$ hz
 $\phi_b = -97.96$ ppm (q.d) $J_{ab} = 18.9\text{hz}$, $J_{bc} = 12.81\text{hz}$

d. $\phi\text{CFCl}_3 \equiv 0.0\text{ppm}$; 1.0% $\text{CFCl}_3/99\%$ CDCl_3 ; $\delta\text{CHCl}_3 \equiv 7.25\text{ppm}$.

e. V. I. Golikov, A. M. Aleksandrov, L. A. Alekseeva, and L. M. Yagupol'skii,
Zhurnal Organicheskoi Khimii, 1974, 10, 297-99 (In Translation UDC 7.412.22
 + 463.4).

TABLE B (CONTINUED)(4)

2,3-Difluoro-2-methylbutane:

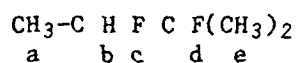
Infrared (cm^{-1}): 3000(s), 2950(m), 1465(m), 1385(s), 1170(s), 1120(s), 1085(s), 960(m), 865(m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 107 (2.1) $\text{C}_5\text{H}_9\text{F}_2$; 89 (100) $\text{C}_5\text{H}_{10}\text{F}$; 69 (9.6) C_5H_9 ,
61 (1.7) $\text{C}_3\text{H}_6\text{F}$.

EI (70eV): 93 (13.0) $\text{C}_4\text{H}_7\text{F}_2$; 79 (25.6) $\text{C}_3\text{H}_5\text{F}_2$; 61 (100) $\text{C}_3\text{H}_6\text{F}$;
60 (17.7) $\text{C}_3\text{H}_5\text{F}$; 47 (14.4) $\text{C}_2\text{H}_4\text{F}$.

$^{19}\text{F} + ^1\text{H}$ NMR^{d,e}



$\delta_a = 1.32$ (d•d•d)	$J_{ab} = 6.6$ hz
$\delta_b = 4.47$ (d•q•d)	$J_{ac} = 23.2$ hz
$\delta_e = 1.34$ (d•d)	$J_{ad} = 1.0$ hz
$\phi_c = -151.60$ (d•d•hept.)	$J_{bc} = 47.6$ hz
$\phi_d = -184.32$ (m•d•q•d)	$J_{bd} = 12.7$ hz
	$J_{cd} = 9.8$ hz
	$J_{ce} = 2.0$ hz
	$J_{de} = 21.5$ hz

d. $\phi\text{CFCl}_3 \equiv 0.0\text{ppm}$; 1.0% $\text{CFCl}_3/99\%$ CDCl_3 ; $\delta\text{CHCl}_3 \equiv 7.25\text{ppm}$.

e. W. J. Middleton, J. Org. Chem., 1975, 40, 574-8. $\phi-152.0$ & -185.5 ppm.

TABLE B (CONTINUED)(5)

2,3,3-Trifluoro-2-methylbutane:

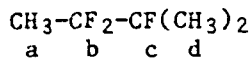
IR (cm^{-1}): 3000(m), 2980(w), 1880(vw), 1485(w), 1390(m), 1260(m),
1170(vs), 1100(w), 1030(w), 940(m), 850(w), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 143 (10.5) $\text{C}_5\text{H}_9\text{F}_3 + \text{CH}_5^+$; 125 (17.0) $\text{C}_5\text{H}_9\text{F}_3$;
107 (100) $\text{C}_5\text{H}_9\text{F}_2$; 89 (24.6) $\text{C}_5\text{H}_{10}\text{F}$; 87 (13.7) $\text{C}_5\text{H}_8\text{F}$.

EI (70eV): 111 (3.6) $\text{C}_4\text{H}_6\text{F}_3$, M- CH_3 ; 95 (8.3) $\text{C}_4\text{H}_9\text{F}_2$; 93 (16.2)
 $\text{C}_4\text{H}_7\text{F}_2$; 69 (15.3) C_5H_9 , CF_3 ; 65 (51.9) $\text{C}_2\text{H}_3\text{F}_2$;
61 (100) $\text{C}_3\text{H}_5\text{F}$; 47 (15.6) $\text{C}_2\text{H}_4\text{F}$; 43 (17.5) C_3H_7 , C_2F ;
41 (19.2) C_3H_5 .

^{19}F and ^1H NMR^d



$\delta_a = 1.65$ (t·d)

$J_{ab} = 18.05$ hz (^1H), $J_{ac} = 1.95$ hz

$\delta_d = 1.737$ (d·t)

$J_{cd} = 21.73$ hz (^1H), $J_{bc} = 1.22$ hz

$\phi_b = -105.70$ ppm (q)

$J_{ab} = 18.3$ hz (^{19}F)

$\phi_c = -154.21$ ppm (heptet)

$J_{cd} = 21.36$ hz (^{19}F)

d. $\phi_{\text{CFCl}_3} \equiv 0.0$ ppm; 1.0% CFCl_3 , 99% CDCl_3 ; $\delta_{\text{CHCl}_3} = 7.25$ ppm.

TABLE B (CONTINUED)(6)

1,3,3-Trifluoro-2-methylbutane:

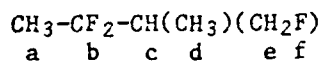
IR (cm^{-1}): 2990(m), 2940(sh), 1750(w), 1470(m), 1400(s),
1300(sh,m), 1250(s), 1215(s), 1170(s), 1110(vs),
1040(s), 990(m), 930(s), 870(sh,m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 143 (12.9) $\text{C}_5\text{H}_9\text{F}_3 + \text{CH}_5^+$; 125 (60.4) $\text{C}_5\text{H}_8\text{F}_3$; 123 (19.3)
 $\text{C}_5\text{H}_6\text{F}_3$; 107 (100) $\text{C}_5\text{H}_9\text{F}_2$, 89 (54.6) $\text{C}_5\text{H}_{10}\text{F}$; 87 (63.1)
 $\text{C}_5\text{H}_8\text{F}$.

EI (70eV): 93 (10.4) $\text{C}_4\text{H}_7\text{F}_2$; 78 (25.6) $\text{C}_3\text{H}_4\text{F}_2$; 77 (23.2) $\text{C}_3\text{H}_3\text{F}_2$;
69 (86.4) C_5H_9 ; 65 (100) $\text{C}_2\text{H}_3\text{F}_2$; 61 (18.4) $\text{C}_3\text{H}_6\text{F}$.

^{19}F and ^1H NMR^d



$\delta_a = 1.60$ ppm (t)

$J_{ab} = 19.05$ hz

$\delta_c = 1.5$ - 2.0 ppm (broad multiplet)

$\delta_d = 1.10$ ppm (d)

$J_{de} = 6.83$ hz

$\delta_e = 4.5$ ppm (d•m)

$J_{ef} = 47.37$ hz (^1H)

$\phi_b = -95.5$ ppm (m)

$\phi_f = -226.77$ ppm (t•d)

$J_{ef} = 47.3$ hz (^{19}F), $J_{cf} = 21.37$ hz

APPENDIX II

Distribution List

TECHNICAL REPORT DISTRIBUTION LIST. GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
		Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST. 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. N. Grimes Department of Chemistry University of Virginia Charlottesville, Virginia 22901	1	Dr. B. Forman Department of Chemistry Brandeis University Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne Department of Chemistry University of California Los Angeles, California 90024	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. D. B. Brown Department of Chemistry University of Vermont Burlington, Vermont 05401	1	Dr. J. Zuckerman Department of Chemistry University of Oklahoma Norman, Oklahoma 73019	1
Dr. D. Venezy Chemistry Division Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Professor G. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. J. Adcock Department of Chemistry University of Tennessee Knoxville, Tennessee 37916	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02157	1
Dr. A. Cowley Department of Chemistry University of Texas Austin, Texas 78712	1	Professor R. Neilson Department of Chemistry Texas Christian University Fort Worth, Texas 76129	1
Dr. W. Hatfield Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1	Professor M. Newcomb Texas A&M University Department of Chemistry College Station, Texas 77843	1
Dr. D. Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor Richard Eisenberg Department of Chemistry University of Rochester Rochester, New York 14627	1
Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1		

